Letters to the Editor

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A study of the structures of calcium chromate

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Single Crystal of $Ca_3(CrO_4)_2$ was obtained by blending stoichiometric amount of $CaCO_3$ and Cr_2O_4 and firing at 950°C for four hours, regrinding and further firing of sixty four hours. The unit cell dimensions were determined by rotation and Weissenberg photographs and the accurate cell dimensions, $a = 10\,75 \pm 0.002$Å and $c = 38\,091 \pm 0\,04$Å were obtained by extrapolation method (Lipson & Steeple 1946). Integrating equi-inclination Weissenberg photographs were taken with Cu K radiation (from Philips X-ray tube) of all the layers about the a axis using the multiple film technique of Robertson (1943). A total of 1160 reflections were recorded which reduced to 664 symmetry independent reflections. The intensities of the integrated Weissenberg reflections were measured with a photometer (Jeffery 1963) and very weak reflections were measured by eye estimation against an intensity scale The intensity data were placed on single scale by correlating the common reflections occurring in the films. Corrections to the intensities were made due to LP factor and absorption. The diameter of the spherical crystal used measured 0.022 cm and μ_R was 5.00 It is estimated that the above error in the intensity measurement was less than 10%. A Laue photograph shows that it must belong to one of the point groups having diffraction symmetry 3m. The density of the crystal as measured by a floation method was 3.22 ± 0.01 gm/c.c. The number of molecules per unit cell is 21 and the calculated value of density fo 21 molecules in the unit hexagonal cell is 3 22 gm/c.c. The comparison with results of intensity statistics (Howells, Phillips & Rogers 1950) together with that obtained from physical tests (pyro and piezo electric effects) confirms that calcium chromate does not possess a centre of symmetry The following systematic absence of reflections was observed.

$$hkil: \quad -h+k+1 = 3n \pm 1, \; h\bar{h}0l : l = 2n \pm 1$$

Since the crystal does not possess a centre, the only possible space group is R3c.

STRUCTURE

Geometrical and intensity comparisons prove beyond doubt that mineral whitlockite (Mackay 1952) and calcium chromate are isomorphous and both

of them can be derived from $Ba_3(PO_4)_2$ structure (Zachariasen 1948). A close relationship between the structure of $Ca_3(CrO_4)_2$ and $Ca_3(AsO_4)_2$ also exists (Gopal & Calvo 1971). The (*hoh*l) Fourier Projection and the following three dimensional

Table 1. Observed and computed $Q_{hkl}\left(=\frac{1}{d^2_{hkl}}\right)$ values of $Ca_3(CrO_4)_2$

(Powder Method)

Indices h	k	l	$d_{(obs)}$	$Qhkl_{(obs)}$	$Qhkl_{(cal)}$	Indices h	k	l	$d_{(obs)}$	$Qhkl_{(obs)}$	$Qhkl_{(cal)}$
1	0	2	8.3713	0.0143	0 0143	2	2	0	2.7044	0 1368	0.1382
1	0	4	6.7270	0.0221	0.221	3	0	8			0.1478
1	1	0	5 3953	0.0344	0 0346	0	1	14	2 6074	0.1471	0.1476
2	0	2	4.5456	0.0484	0 0488	2	1	13	2 2491	0.1977	0.1971
1	0	8			0 0556	4	1	3	2.0022	0.2495	0.2481
2	0	4	4.2316	0 0558	0.0571	2	2	15	1.8441	0.2941	0.2932
2	1	7	3 5349	0.0800	0.0806	3	3	3	1.7748	0.3174	0.3172
2	1	4			0 0916	3	1	17	1 6925	0 3491	0.3489
2	0	8	3.3148	0.0910	0.0902	4	2	11	1 5706	0.4054	0 4059
1	1	9			0 0904	4	3	1			0.4269
3	0	4			0 1147	3	1	20			0.4253
2	1	7	2 9598	0 1141	0 1144	6	0	4	1 5313	0 4264	0 4257
0	2	10			0 1148	5	1	10			0 4260

Patterson syntheses confirmed the above observations —Sections at (i) $Z = 0$ (ii) $Y = 0$ (iii) $Y = \frac{1}{2}$, $X+Y = 1$ and Patterson difference Section at $X+Y = 1$. From the similarities in the symmetries and distribution of spot intensities in the X-ray diffraction photographs of the two crystals, viz $Ca_3(CrO_4)_2$ and $Ca_3(AsO_4)_2$, the atomic co-ordinates were chosen.

The probable atomic parameters are listed in Table 2. The value of R for this model for $ho\bar{h}$l reflections was 0.14.

Table 2 Atomic co-ordinates of $Ca_3(CrO_4)_2$

Atoms	Site of summetry	X	Y	Z	Atoms	Site of symmetry	X	Y	Z
Cr(1)	3	0	0	0	O(2)	1	0.15	0.25	0.16
Cr(2)	1	0.33	0 16	0 16	O(3)	1	0.25	0.00	0.16
Cr(3)	1	0.33	0.16	0.25	O(4)	1	0.50	0.25	0.16
Ca(1)	1	0.25	0.168	−0.168	O(5)	1	0.50	0.04	0.25
Ca(2)	1	0.33	0 16	0.04	O(6)	1	0.50	0.33	0.25
Ca(3)	1	0.25	0 16	−0 04	O(7)	1	0.16	0.08	0.25
Ca(4)	3	0	0	0.25	O(8)	1	0.33	0.16	0.25
Ca(5)	3	0	0	0.084	O(9)	1	0	0.16	0.05
O(1)	1	0 25	0 084	0.084	O(10)	3	0	0	−0.04

Further structural details will be published in due course.

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Anharmonicity of lattice dynamics of sodium fluoride

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In recent years, considerable interest has been shown by a number of authors, including Krivoglaz & Tekhonova (1961), Hahn & Ludwig (1961), Maradudin & Flinn (1963) and Kashiwase (1965) on the calculations of cubic-anharmonic and quartic-anharmonic contributions to the Debye-Waller factors. Hahn & Ludwig have studied the effect of anharmonic vibration on the thermal scattering of X-rays from crystals for temperatures above the Debye temperature. In their theory, the effect was given in terms of the temperature dependent dispersion relation in place of the temperature independent dispersion relation which was used in the usual formula of X-ray thermal scattering by crystals. Maradudin & Flinn (1963) have considered a non-atomic crystal with atoms arrayed at the points of a cubic Bravis lattice and obtained contributions proportional to the square and the cube of the absolute temperature in the classical limit. Their calculations are extremely lengthy and nowhere correlated with the experiments. Quite recently, Willis (1969) has made a different approach by treating the crystal as an Einstein solid whereby each atom vibrates in a potential field which is not affected by the motion of the neighbouring atoms. He extended the analysis to the rock salt, diamond, and fluorite type structures and obtained good agreements with experiments in KCl and BaF_2. The theory has further been applied by the authors to investigate the effect of lattice anharmonicity on on the Debye-Waller factors of KBr and has been found to show good agreement with experiments

In the present note, we have applied the same technique to sodium fluoride. Following Willis, the isotropic B-factor of x-ion at temperature T is given by

$$B_X(T) = \frac{8\pi^2 K_B T}{\alpha_{0X}} \left[1 + T(2\psi\gamma_G - 20K_B \frac{\gamma_{uX}}{\alpha^2_{0X}} \right], \qquad (1)$$